5-29-1929

A Study of the Oxidation of d-Glucose with Air in a Saturated Solution of Barium Hydroxide

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A STUDY OF THE OXIDATION OF d-GLUCOSE WITH AIR IN A SATURATED SOLUTION OF BARIUM HYDROXIDE

BY

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A THESIS

Presented to the Faculty of

The Graduate College in the University of Nebraska

in Partial Fulfillment of Requirements

for the Degree of Master of Science

Department of Chemistry

Lincoln, Nebraska

May 29, 1929

The author wishes to express his sincere gratitude for the interest and aid of Dr. F. W. Upson, under whose direction this research was carried out.

TO MY PARENTS

who thru their sacrifices

have made possible my

education

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I
INTRODUCTION

The structural arrangement and oxidation of the simple sugars has been the object of study and investigation of such men as Emil Fischer, Nef, Hudson, Anderson, Kiliani, Evans, Spoehr and a host of others. From their results have come very definite and conclusive evidence concerning the relationship among the simple sugars and the oxidation products under controlled conditions.

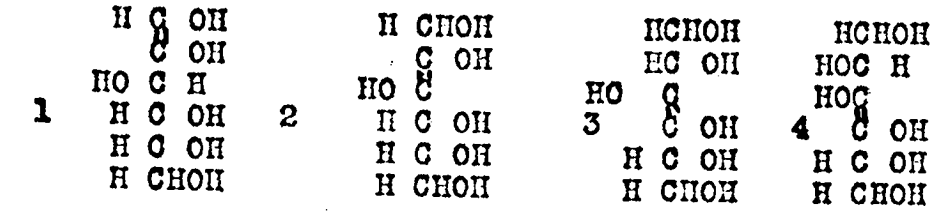
The conversion of one aldose into another aldose and several ketoses slowly by weak alkalis at ordinary temperatures and quickly with much decomposition at elevated temperatures, was first observed by Lobry de Bruyn(1) and later investigated by Nef and his students(2) in an elaborate study on the action of strong alkalis alone and with oxidizing agents extending over a period of ten years. The results of these studies on oxidation were interported as depending on the presence of several intermediate enediols. The oxidation of sugrs in

approximately six normal alkali medium with air or oxidizing agents all give about the same general results in regard to the sugar destroyed, non-volatile and volatile acids produced. In these oxidations the concentration of the -OH ion decreases as the reaction proceeds. To the present time but one study on the products of oxidation of the simple sugars in an alkaline solution having a fairly constant -OH ion concentration has been reported(3); that of Powers using lime water. In this work the oxidation products only were studied and not the rate of oxidation. The present work was started to study the rate of such an oxidation, because of the bearing it might have on the explination of the animal oxidation where the body maintains exacting degrees of acidity and alkalinity.

II
THEORETICAL DISCUSSION

As has been mentioned above, according to Nef, the various hexose sugars are oxidized by the splitting of the various unsaturated 1-2, 2-3, 3-4 enediols which are formed in alkaline solution. In a glucose solution of the concentration used, there is a

possibility, according to Nef, of the four following enediols being formed:



1-2-enediol 2-3-enediol α- and β-3-4-enediols

These ensdiols being unsaturated react like many other compounds containing an unsaturated carbon chain and break apart spontaneously at the double bond forming two methylene chains which are capable of internal rearrangement to form aldehydes, recondense with each other, or if oxygen is present, be oxidized directly to the acids. All of the oxidation products that have been isolated can be accounted for by the splitting and subsequent immediate oxidation of the four enediols given above. The following oxidation products are found under similar conditions as the present investigation: formic acid, HCOOH; glycolic acid, HCH(OH)COOH; dl-glycerinic acid, HCH(OH)HC(OH)COOH; arabonic acid, HCH(OH)-$(HCOH)_3COOH$; l-theronic acid, HCH(OH)$(HCOH)_2COOH$; d-erthronic acid, HCH(OH)$(HCOH)_2COOH$; and small amounts of carbon dioxide, CO_2 and mannonic and

gluconic acids. From the results of previous workers(4) it is evident that the relative amounts of the different oxidation products may very somewhat depending upon a number of factors such as concentration of alkali, temperature, the oxidizing agent (hydrogen peroxide, air, Fehling's solution, silveroxide, etc.) and the particular sugar used.

It is interesting to note that the various workers(4) find that a much larger percentage of the glucose destroyed is converted to the shorter chain oxidation products than the longer chain products. The bearing of these facts on the results found in the present investigation will be discussed under the section on results. In an investigation on the rate of oxidation of various sugars with air in NaOH solution by R.V.McGrew(5) and E.J. Boschult(6) at temperatures of 0°, 15° and 25° and 40° C., respectively, it was found that the rate of formation of the volatile and non-volatile acids produced to the mols of volatile acids produced and the ratios of mols of volatile, non-volatile and total acids produced to the mols of sugar destroyed are constant thru-out the reaction, hence there is "probably no appreciable accumulation of intermediate products at any

time during the reaction". They also found that approximately two mols of acids were formed for each mol of sugar destroyed, and that this indicated that a "part of the sugar must undergo more than one spliting".

The question now arises as to the effect of constant -OH ion concentration on the course of the reaction at different temperatures. With a view to study this point, the present investigation was undertaken. Barium hydroxide was chosen because it gave approximately a .5 N saturated solution at 25°. Air was used as an oxidizing agent. 25° and 40° C. were chosen for comparison with previous work(6).

III
EXPERIMENTAL PART

A. Apparatus Used

The apparatus used in studying the oxidation of d-glucose in barium hydroxide solution by air is illustrated in Figure I. Air was forced from the air line thru a series of bottles containing concentrated H_2SO_4 to free it from moisture and impurities, then thru towers of soda-lime, thru a spiral coil and into the oxidation bottle. From the oxidation

bottle the escaping air was carried thru a condenser to condense any vapors that might be carried off during the oxidation, thus maintaining the oxidation mixture at a constant volume. The spiral coil and the oxidation bottle were immersed in a constant temperature bath (not shown in the Figure). Over a period of seven hours, readings taken every 15 minutes showed a maxium variation of the temperature of .13° C. from the given temperature. The end of the capillary tubing which was immersed in the oxidation bottle was enlarged and filled with glass wool as shown in Figure I. With this precaution, a sample could be taken that was free from solid $Ba(OH)_2$.

B. Reagents Used

The sugar used in the present investigation was Mallinckrodt's "C. P. Dextrose Anhydrous". Merk's crystalline "C. P. Barium Hydroxide" was used. The acids and bases used in the determination of the volatile and non-volatile constituents were made from standard reagents of "C. P." quality.

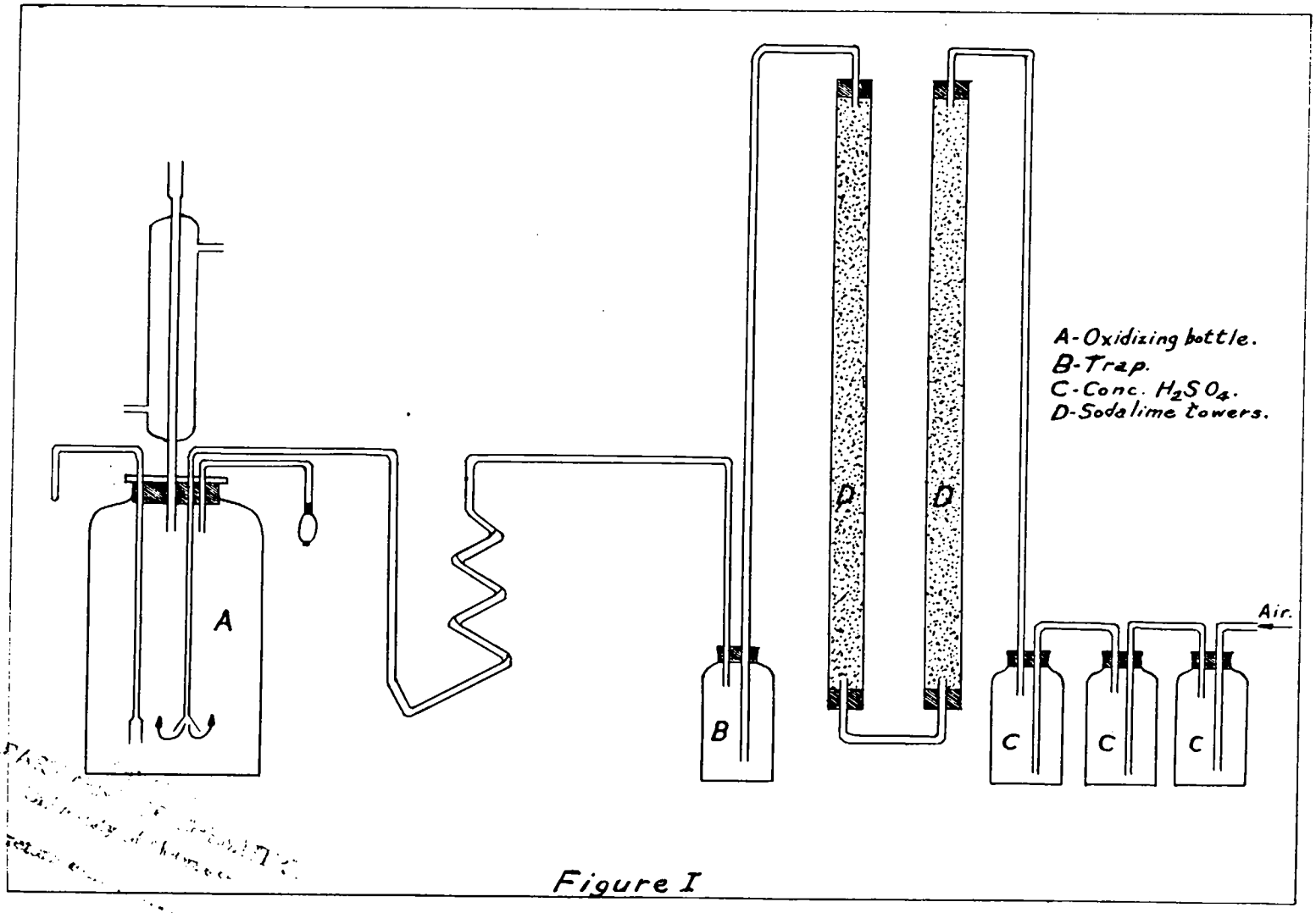

A-Oxidizing bottle.
B-Trap.
C-Conc. H_2SO_4.
D-Soda lime towers.
A
B
D
D
C
C
C
Air.

Figure I

C. Preparation of Oxidation Mixture

All of the preparations for the mixtures were made in the following manner: two l's of saturated $Ba(OH)_2$ were placed in the oxidation bottle. In the case of the investigations at 25°, 600gms, and at 40°, 1000 gms. of solid crystalline $Ba(OH)_2$ were added. This excess solid crystalline $Ba(OH)_2$ insured a saturated solution throughout the entire run of each investigation.

A sample of d-glucose weighing exactly 52.5000 gms. (17.5000 gms. per liter of oxidation mixture) was dissolved in distilled water and made up to a l. of solution. Both solutions were placed in a bath at the given temperature and allowed to reach equilibrium. Eight minutes before the first sample called No. 0, was to be taken the sugar solution was placed in the oxidizing bottle and allowed to reach equilibrium. The sample 0 was immediately forced thru the capillary tubing into a caliberated flask and the various proceedures carried out as was necessary to determine the reducing sugars present, the non-volatile and volatile acids produced. This proceedure is given under the proper sections.

IV
ANALYSIS AND CALCULATION

A. Determination of total Ba^{++}

At each reading, two samples of the oxidation mixture, each of which were forced into a 25° cc caliberated flask, were titrated with N H_2SO_4, and a slight excess was added. These were filtered, ignited, weighed and calculated for total Ba^{++} present per cc of solution at 25° C. Equivalent cc's. of N HCl per 50 cc sample, and milimols Ba^{++} per cc solution are calculated from these readings and are listed in Table I, page 9. The values of column 5 and 6 were calculated from the curves obtained by plotting the values of column 4. Similar calculations for the total grams of Ba^{++} cc's of N HCl at 40° C. are given in Table II, page 10. The results of Table I and II are plotted in Figure II and III, respectively.

B. Determination of Volatile Acids

The volatile acids were determined on a 50 cc. sample by first neutralizing the free $Ba(OH)_2$ with N HCl and then adding N HCl equal to the

TABLE I

1	2	3	4	5	6
No	Hrs. of Run	grms. of $BaSO_4$ / cc solution	grms. of Ba^{++} / cc solution	millimols Ba^{++} / cc of solution	cc's N HCl equal to grms. of Ba / cc solution
1	0	.0316	.0186	.1359	13.54
2	3	.0419	.0247	.1798	17.98
3	4	.0497	.0297	.2156	21.56
4	6	.0555	.0328	.2382	23.82
5	8	.0594	.0350	.2551	25.51
6	10	.0623	.0368	.2671	26.71
7	15	.0675	.0397	.2878	28.78
8	20	.0701	.0412	.2979	29.97
9	24	.0714	.0420	.3060	30.50
10	28	.0726	.0427	.3105	31.05
11	30	.0731	.0430	.3117	31.17
12	34	.0744	.0438	.3189	31.87
13	40	.0770	.0453	.3293	32.86
14	46	.0784	.0461	.3345	33.45
15	52	.0793	.0466	.3386	33.86
16	60	.0799	.0470	.3414	34.14
17	72	.0814	.0478	.3467	34.67
18	88	.0839	.0494	.3588	35.88
19	99	.0848	.0499	.3623	36.23
20	111	.0854	.0503	.3650	36.50
21	129	.0860	.0506	.3677	36.77
22	135	.0864	.0508	.3688	36.88
23	141	.0866	.0509	.3695	36.95

TABLE II

1	2	3	4	5	6
No.	Hrs. of Run	grms. of $BaSO_4$ / cc solution	grms. of Ba^{++}/cc solution	millimols Ba^{++}/ cc solution	cc's N HCl equal to grms. of Ba / cc solution
1	1	.1172	.0378	.494	49.25
2	2	.1233	.0726	.518	53.00
3	4	.1286	.0756	.550	54.22
4	6	.1303	.0769	.560	55.00
5	10	.1331	.0790	.575	57.30
6	13	.1348	.0793	.576	57.50
7	24	.1331	.0790	.574	57.40
8	33	.1363	.0804	.585	58.89
9	48	.1390	.0816	.594	59.30
10	73	.1358	.0800	.582	58.10
11	97	.1410	.0830	.604	60.35
12	120	.1414	.0823	.606	60.50

FIGURE II
OXIDATION OF d-GLUCOSE BY AIR AT 25°

Volatile, Non-Volatile Acids
And Total Ba^{++}

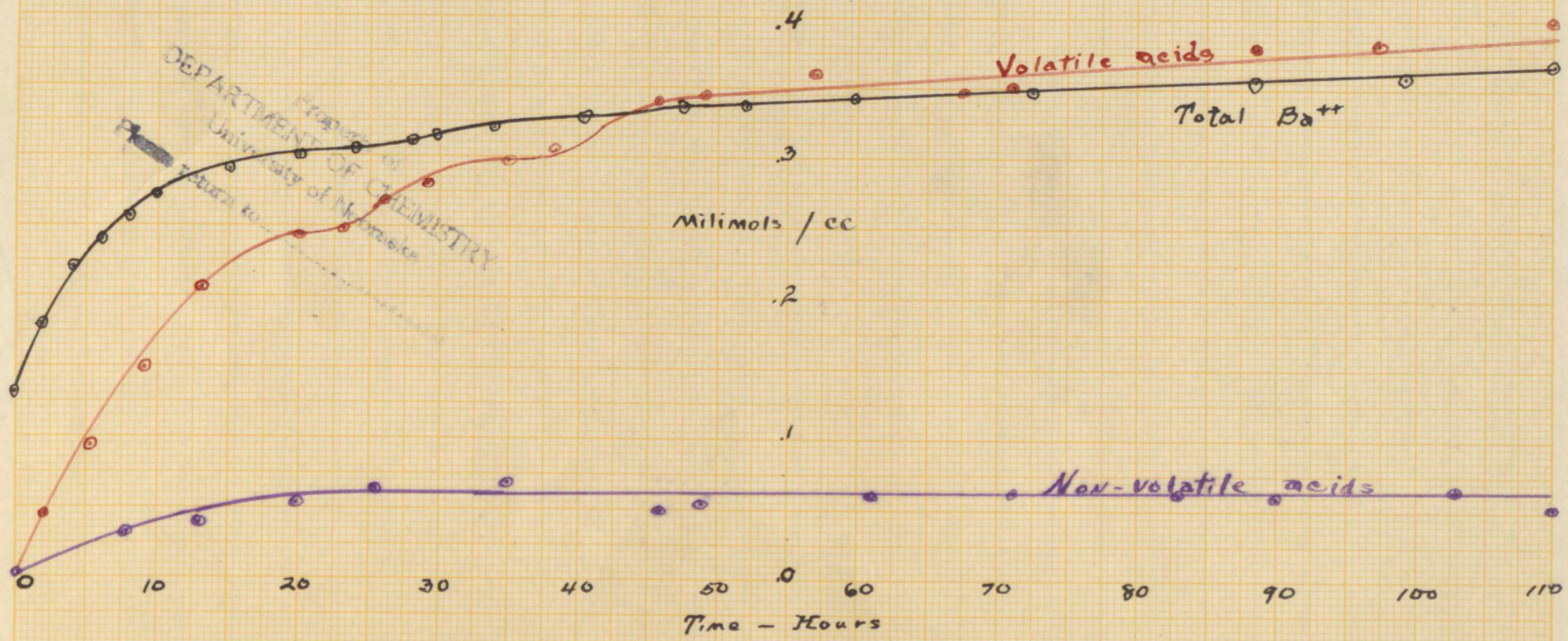
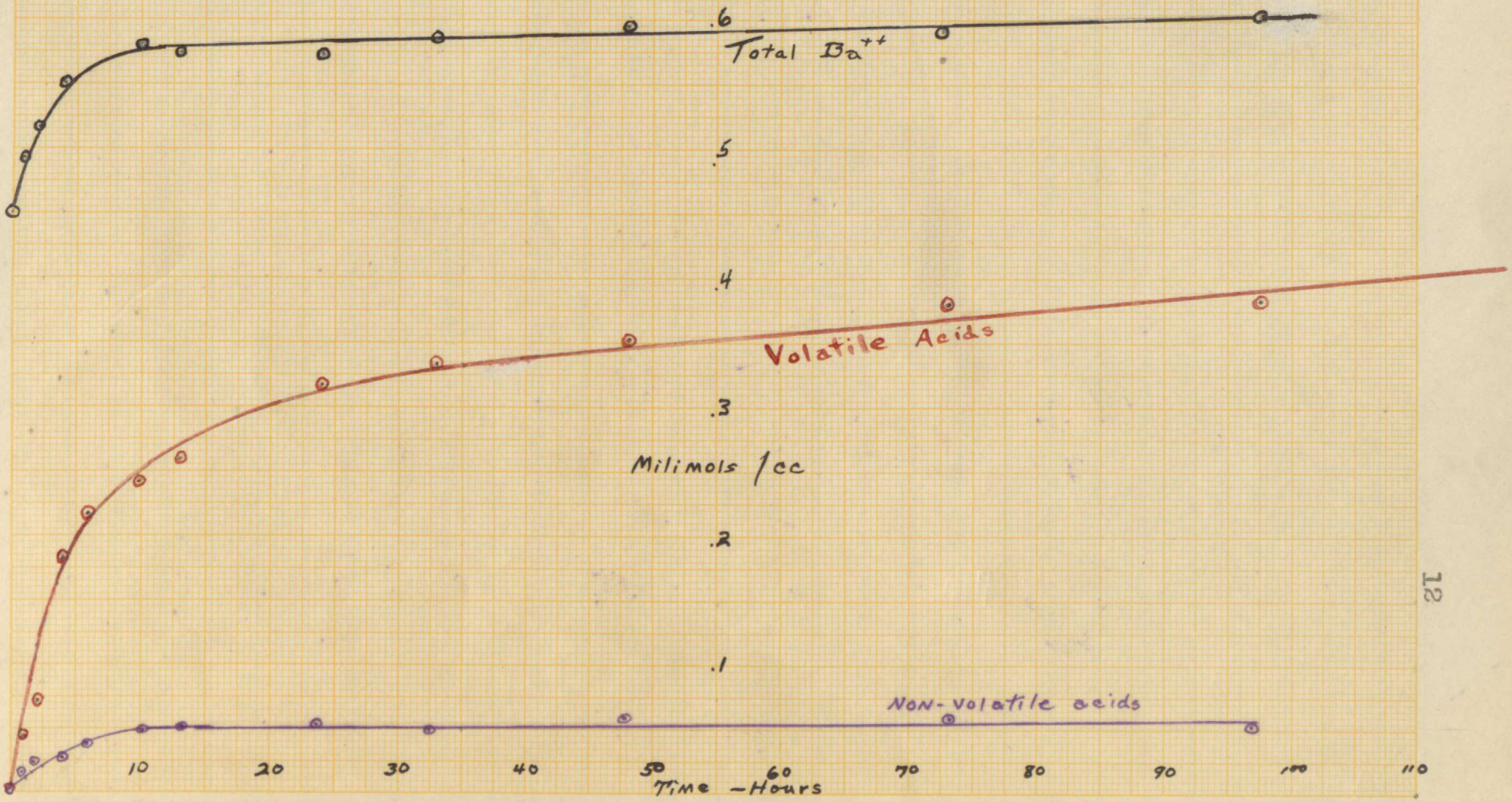


FIGURE III
OXIDATION OF d-GLUCOSE BY AIR AT 40°

Volatile, Non-Volatile Acids
And Total Ba^{++}



difference between the free $Ba(OH)_2$ and the total Ba^{++}. The sample was distilled to dryness at approximately 20 mm and a temperature of 50-60°C. The dry residue was swept over with two successive 20 cc. portions of distilled water.(During the last washing the temperature was raised to boiling.) The entire distillate was drawn thru a measured excess of standard alkali solution.

The total distillate and washings were titrated with N HCl and calculated as formic acid. The air drawn in during the vacuum distillation was freed from CO2. The results of these determinations and the calculated amounts of formic acid produced at 25° and 40°C. are given in Table III and IV respectively. The results found in Table III and IV are plotted in Figures II and III respectively.

C.Determination of Non-Volatile Acids

The excess N HCl added to each 50 cc. sample (25°; Table III, column 4 and 40°; Table IV column 4) represent equivalent cc's N Ba^{++} per 50 cc sample (since 50 cc samples were taken), which are calculated to gms. of Ba^{++} per cc. existing as salts (25°)

Table III, column 5 and 40°; Table IV, column 5) and milimols of Ba^{++} per cc existing as salts (not given in the table). Twice the milimols of Ba as salts gives the milimols of total acids (25°; Table III, column 6 and 40°; Table IV, column 6). The non-volatile acids then are given by subtraction of the milimols of formic acid produced from the milimols of total acid and are shown for 25° in column 11 and for 40° in column 11. (These values for non-volatile acids were derived from plotted values of milimols of total acids thus giving truer values for non-volatile acids). The values for the rate of formation of non-volatile acids are shown in Figure II, page 11 at 25° and Figure III, page 12 at 40° C.

D. Determination of Reducing Sugars

Benedict's method for the quantitative determination of reducing sugars(7) was used. The 50 cc sample taken was first neutralized with N HCl and a slight excess added. All of the samples were then made up to 250 cc, i,e., diluted 5 times. Sample No.0 was used as a basis for all calculations of the amount of reducing sugars in solution per cc,

TABLE III

1	2	3	4	5	6	7	8	9	10	11
Hrs. of Run	N HCl = to total Ba / 50cc sample	N HCl to neut. sample	(2)-(3) = (4) = cc's N Ba = to salts / 50cc. sample	grms. Ba''es salts / cc. solut.	millimol total acids / cc. soln.	cc NaOH in receiving flask	cc N HCl to neut. (7)	cc N V. acids / cc. (7)-(8) =(9)	milli-mols V.Acids / cc. calcul. as formic acid	milli-mols N.-V. acids / cc. soln.
0	13.54	13.4	0.00	.000	.000	2.40	2.40	0.00	.000	.000
2	17.98	15.55	2.45	.00536	.04890	2.40	.241	2.169	lost	
4	21.56	16.82	4.74	.00651	.0948	9.18	6.04	3.14	.0627	.0200
6	23.82	17.20	6.62	.00910	.1326	14.77	7.71	6.06	.1211	.0225
8	25.51	17.97	7.54	.01036	.1508	9.18	2.95	6.23	.1248	.0280
13	28.28	16.13	12.13	.01667	.2424	13.77	3.58	10.19	.2038	.0385
20	29.97	14.81	15.16	.02085	.2922	20.10	7.38	12.72	.2414	.0505
23	30.18	14.27	15.91	.02190	.2940	20.10	7.73	12.37	lost	
26	30.70	14.06	16.64	.02285	.3330	21.10	7.58	13.52	.2704	.0570
29	31.05	13.98	17.07	.02344	.3412	20.10	5.97	14.13	Lost	
35	32.02	13.83	18.19	.02486	.3622	20.10	5.47	14.63	.2926	.0590
46	33.45	13.52	19.93	.02740	.3906	20.10	3.04	17.06	Lost	
49	33.68	13.62	20.06	.02756	.3990	20.10	2.83	17.27	.3454	.060
61	34.16	13.74	20.42	.02806	.4063	22.11	4.63	17.43	.3486	.060
71	34.60	13.90	20.70	.02844	.4140	22.11	4.52	17.59	.3500	.0601
83	35.52	14.08	21.44	.02946	.4294	22.11	3.65	18.46	.3593	.0601
90	35.98	14.02	21.26	.03017	.4390	23.12	4.81	18.31		
111	36.50	13.56	22.94	.03152	.4590	23.12	3.01	20.11		

TABLE IV

1	2	3	4	5	6	7	8	9	10	11
Exp. of Run	N HCl = total Ba / 50cc sample	N HCL to neut. sample	(2)-(3) = (4) = cc's N Ba = to salts / 50cc sample	grms. Ba salts / cc soln.	millimols total acids / cc soln.	cc.N NaOH in receiv-flask	cc. N HCl to neut. (7)	cc.N V. acids / cc (7)-(8) = (9)	milli-mols V. Ac. / cc calcul. as formic acid	milli-mols N.-V. acids / cc soln.
1	49.25	46.10	3.15	.00432	.0648	20.00	17.81	2.19	.0438	.021
2	52.80	48.05	4.75	.00655	.0953	"	16.42	3.58	.0703	.025
4	54.82	44.25	10.57	.01452	.2114	"	10.68	9.32	.1864	.025
6	55.90	43.30	12.60	.01731	.2520	"	9.92	10.80	.2160	.036
10	57.30	42.75	14.55	.01998	.2910	"	7.80	12.20	.2440	.047
13	57.50	42.00	15.50	.02128	.3101	"	6.96	13.04	.2601	.050
24	57.40	38.86	18.54	.02547	.3708	"	4.16	15.84	.3189	.052
33	58.39	39.33	19.06	.02620	.3812	"	3.44	16.56	.3312	.050
48	59.30	38.68	20.62	.02830	.4123	"	2.43	17.57	.3513	.061
73	58.10	36.15	21.95	.03015	.4390	25.00	5.98	19.02	.3800	.059
97	60.35	38.58	21.77	.02992	.4354	"	5.90	19.10	.3824	.053
120	60.50	35.85	24.65	.03385	.4930	"	3.50	21.50	.4300	.063

i.e., the cc's of dilute sugar solution needed to react with exactly 25 cc. of Benedict solution was used as a basis to calculate the milimols of sugar per cc of solution. The initial concentration in every case was 17.5000 grams per liter or.09720 mols per liter.

Some difficulty was encountered in determining exactly the end point of the Benedicts solution when titrated with every dilute sugar solution because the color of the solution changed slowly from blue to purple instead of the usual white percipitation of cuprous sulfocyanate. The average of two, three, and often four titrations were used, although they seldom varied more than a cc.

The cc's Benedict solution used, the cc's of dilute sugar solution used to react with the Benedicts solution, the concentration of the sugar per cc solution and the milimols of sugar destroyed per cc of solution are given in Table V for 25° and 40° C, and are plotted in Figure IV, page 19.

TABLE V

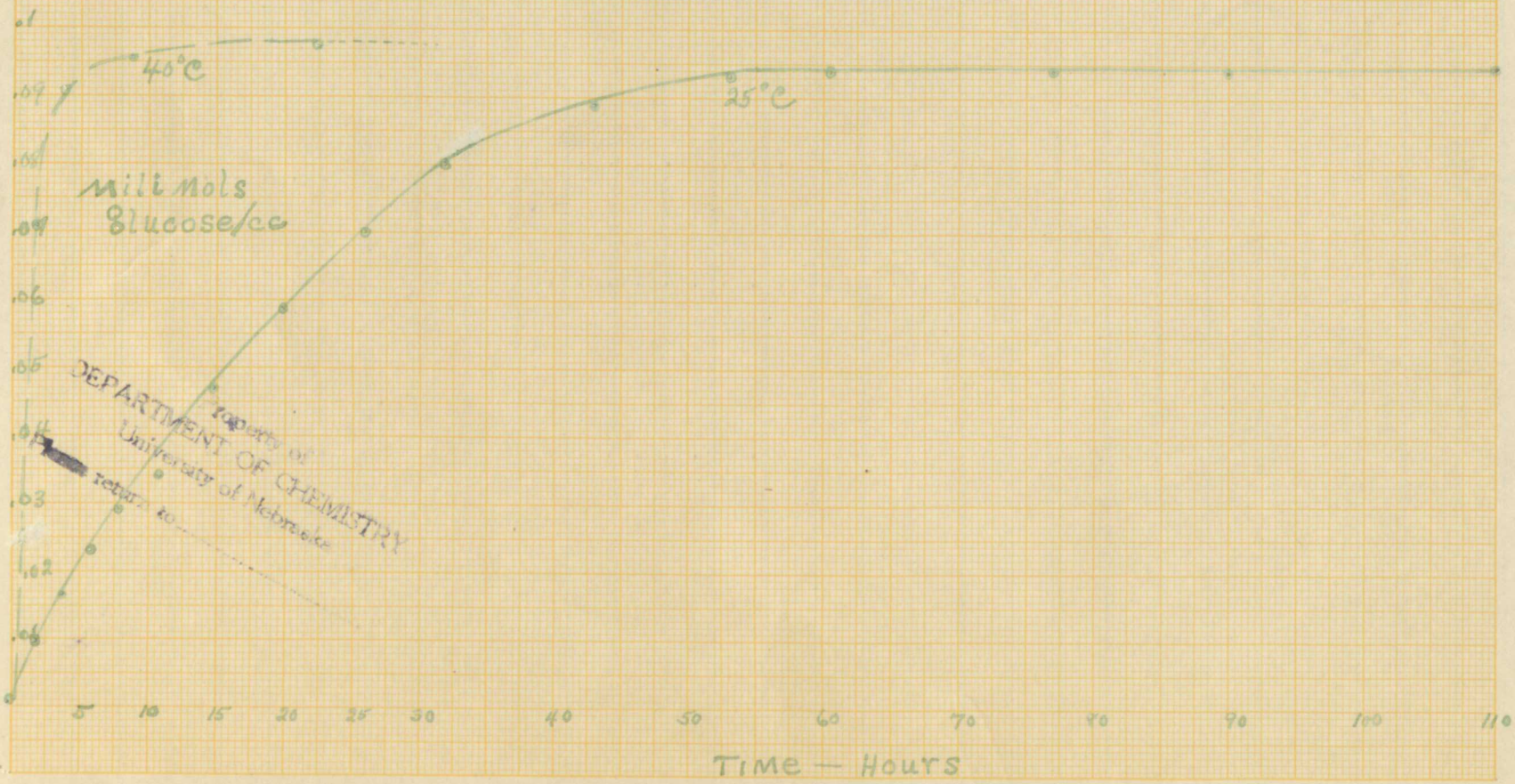
A. Temperature 25° C.

1	2	3	4	5
Hrs of Run	cc's Benedict solution used	cc's dilute sugar solution to react with (2)	milimols sugar per cc.	milimols sugar destroyed / cc solution
0	25	13.88	.09720	.000
2	25	15.32	.0880	.0092
4	25	16.65	.0810	.0162
6	25	18.20	.0745	.0227
8	25	19.54	.0690	.0282
11	25	21.4	.0640	.0332
15	25	26.7	.0505	.0467
20	25	34.6	.0390	.0582
26	25	49.0	.0275	.0697
32	25	74.8	.0180	.0792
43	2.5	76.65	.0088	.0884
53	2.5	140.1	.0046	.0926
61	2.5	168.7	.0040	.0932
77	2.5	177.5	.0038	.0934
90	2.5	197.7	.0035	.0937
111	2.5	232.5	.0029	.0944

B. Temperature 40° C.

0	25	13.67	.09720	.0000
2	25	50.5	.02716	.07004
4	2.5	17.0	.00645	.09072
9	2.5	60.0	.00222	.09498
23	.625	19.5	.00034	.09686

FIGURE IV
OXIDATION OF d-GLUCOSE BY AIR AT 25° AND 40°



E. Completness of Reaction

The percentage completness of the reaction were calculated and plotted to gain some idea as to the velocity and character of the oxidation products. The milimols of the non-volatile and volatile acids produced at the end of the run were used as a basis for calculation. The initial concentration of sugar (.09720 milimols per cc) was used as a basis for the percentage completion of glucose destroyed. The values are given for 25° in Table VI, page 21 and plotted in Figure V. For 40° the values are given in Table VII, page 22 and plotted in Figure VI.

F. Determination of Ratio of Acids to Sugar Destroyed

The determination of the ratios of mols of acid produced to mols of sugar destroyed are given in Table VIII, page 24 for 25° and 40° and are calculated from the curves in Figures II and IV for 25° and from the curves in Figures III and IV for 40°. The ratios of mols of volatile and non-volatile acids produced at a given time to the mols of glucose destroyed is given in Table IX.

TABLE VI-25°

	Glucose destroyed. .09720 millimols / cc at start		Millimols formic acid produced. .4166 millimols at end of run		Non-Volatile acids produced. .0305 millimols at end of run	
1	2	3	4	5	6	7
Hrs. Run	.0972 - x = millimols of (2)	(2)x100 / .0972 = % complete	.4166 - x = (4)	100% - (4)x100 / .4166 = % complete	.0305 - x = (6)	100% - (6)x100 / .0305 = % complete = (7)
0	.0000	00.0%	.417	00.0%	.0305	00.0%
2	.0092	9.46	.374	10.2	.	
4	.0162	16.20	.353	15.2	.0405	53.1
6	.0227	23.30	.296	28.3	.0380	37.2
8	.0282	29.0	.292	29.8	.0325	47.2
13	.0417	42.9	.215	48.8	.0220	63.6
20	.0582	59.9	.176	57.7	.0100	83.5
35	.0922	84.8	.124	70.2	.0015	97.5
46	.0902	93.8	.076	81.7	.	
49					.0005	99.2
57	.0931	95.8	.061	82.3		
61	.0932	95.9			.0005	99.2
83	.				.0004	99.3
90	.0937	96.5	.037	91.1		
120	.0949	97.7	.018	95.7	.0000	99.5

TABLE VII

	Glucose destroyed. .09720 millimols / cc ar start of run.		Millimols formic acid produced .4300 millimols at end of run		Non-Volatile acids produced .063 millimols at end of run	
1	2	3	4	5	6	7
Hrs of Run	.0972- x = millimol of (2)	$\frac{(2)x\ 100}{.0972}$ = % complete	.430 - x = (4)	$\frac{100\%-(4)x100}{.430}$ = % complete	.0605 - x= (6)	$\frac{100\ \%\ (4)x100}{.0630}$ = (7) = % complete
0	.0000	00.0%	.430	00.0%	.063	00.0%
2	.07004	72.0	.360	16.3	.420	33.3
4	.09072	93.3	.244	43.2	.038	39.5
6			.214	52.5	.0376	40.2
9	.09498	97.7	.		.027	57.1
10			.186	56.7	.016	74.6
13			.170	60.5	.013	79.4
24	.09669	99.6	.112	74.0	.011	82.5
33			.099	77.0	.010	84.1
48			.080	81.4	.008	87.3
73			.050	88.4	.006	90.5
97			.048	89.0	.002	96.8
120			.000	---	.000	---

FIGURE V
OXIDATION OF d-GLUCOSE BY AIR AT 25°

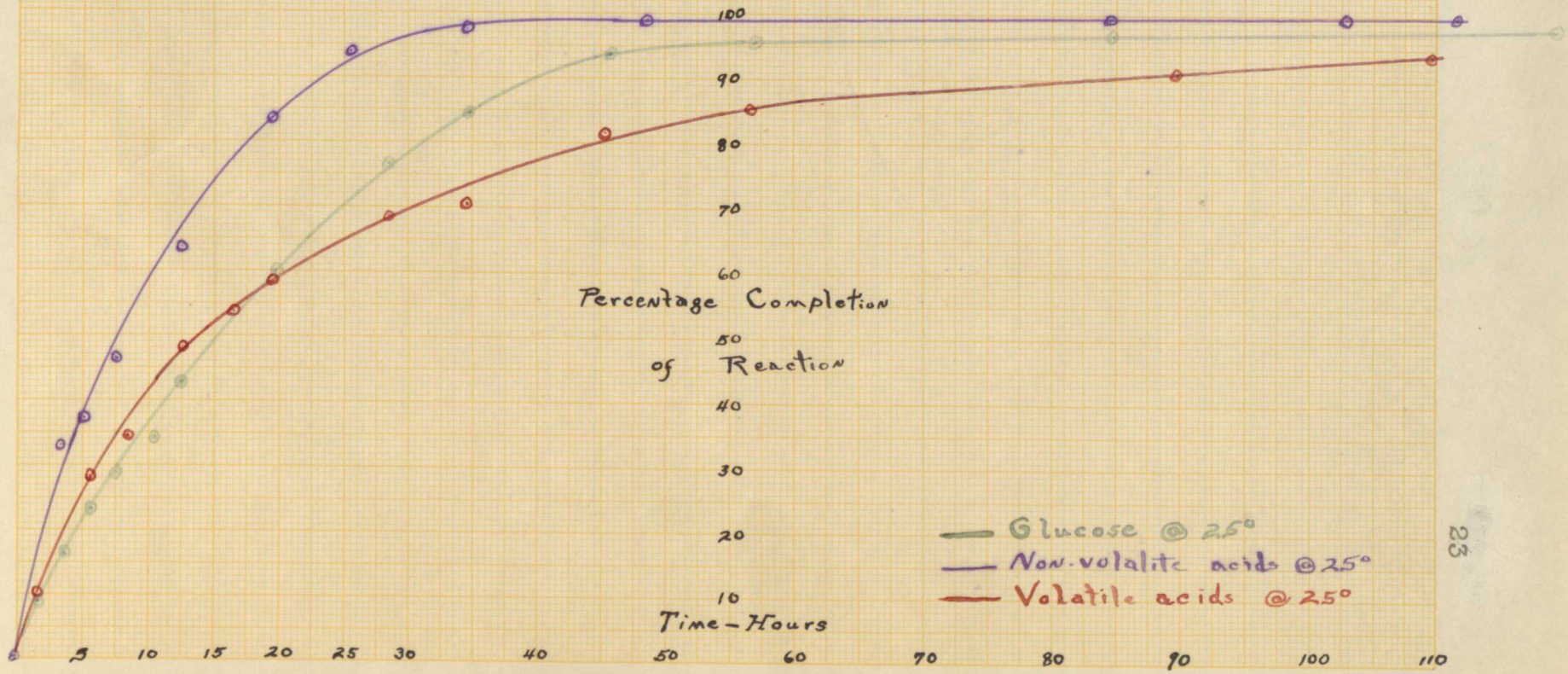


FIGURE VI
OXIDATION OF d-GLUCOSE BY AIR AT 40°

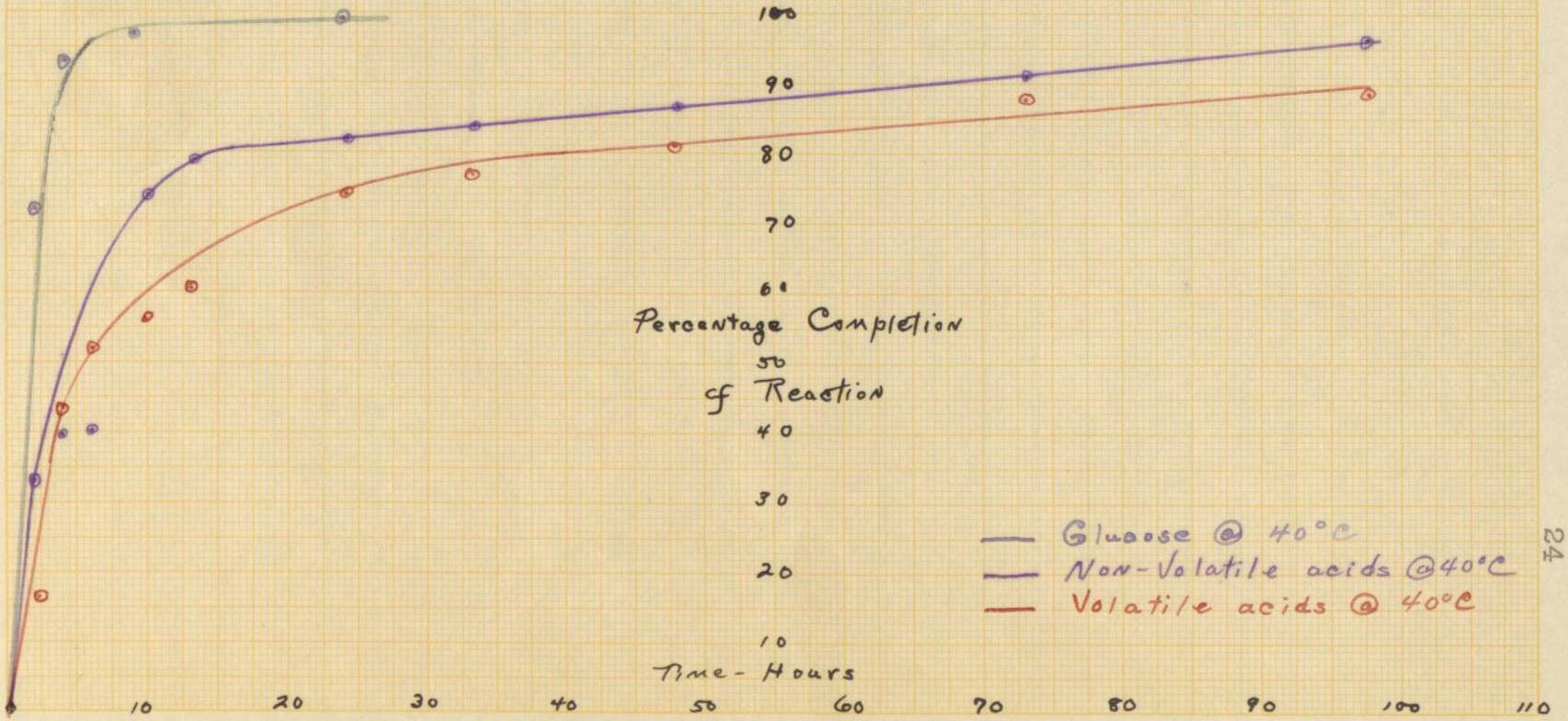


Table VIII

Temp.	Millimols at end of run of—			Ratio of—	
	Glucose destroyed	Non-Vol. acids produced	Vol. Acids produced	N.-Vol. Ac. to sugar destroyed.	Vol.Ac. to sugar destroyed.
25	.0049	.0605	.4166	.639	4.40
40	.0969	.0630	.4300	.652	4.45

Table IX.

A. Temperature 25° C.

1	2	3	4	5	6
Determination	Milli-mols glucose destroyed	Milimols Vol. acids produced	Ratio vol.acid to sugar dest.	Milimols non-v. acids produced	Ratio n-vol. acids prod. to sug. dest.
1	.01	.036	3.6	.003	.3
2	.02	.077	3.9	.017	.9
3	.03	.133	4.4	.026	.9
4	.04	.180	4.5	.036	.9
5	.05	.210	4.2	.043	.9
6	.06	.258	4.3	.048	.8
7	.07	.262	3.8	.054	.8
8	.08	.286	3.6	.058	.7
9	.09	.314	3.5	.060	.7
10	.1	.416	4.2	.060	.6
		average	4.02	average	.8

B. Temperature 40° C.

1	.01	.025	2.5	.006	.5
2	.02	.030	1.5	.007	.35
3	.03	.049	1.6	.003-	.27
4	.04	.060	1.5	.009	.22
5	.05	.070	1.4	.010	.20
6	.06	.078	1.3	.015	.22
7	.07	.095	1.4	.015	.21
8	.08	.135	1.7	.020	.25
9	.09	.263	2.9	.030	.33
10	.1	.330	3.3	.051	.50
		average	1.91	average	.305

C. Determination of Residue from Oxidation Runs

The excess air from the oxidation (Figure I) was carried thru the condenser and bubbled into a saturated solution of $Ba(OH)_2$ (not shown in the Figure). During the course of the runs only a slight turbidity developed and it was thought that possibily if any CO2 was formed it might be percipitated as insoluble $BaCO_3$. Accordingly the residues were boiled to dissolve as much of the $Ba(OH)_2$ as possible and filtered hot, washed thoroughly a number of times with hot water to remove the last trace of $Ba(OH)_2$, dried and calculated roughly for CO_2.

No	Temp	gms. of $BaCO_3$	Calculated	Found	% of residue CO_2
1	25	1.1843	.2642	.2278	86.1
2	25	2.1287	.4690	.3930	84.2
				average	85.15%
1	40	.9380	.2085	.1673	80.0
2	40	1.0677	.8725	.828	85.5
				average	82.8%

At 25° an average of 12.3930 gms. of $BaCO_3$ / 1. was found or 2.360 gms. of CO_2. At 40° an average of 21.815 gms. of $BaCO_3$ per 3 liters was found, which is equivalent to 1.342 gms. of CO_2 or .0303 mols per liter of solution. If all the glucose (17.5000 grams) was converted to CO_2 there would be a possibility of 25.65 gms. or .582 mols of CO_2 per 1. Thus at 25° there is approximately 9.20% of the theoretical converted to CO_2 or for every mol of sugar destroyed, .092 mols of CO_2 is produced, calculated on the basis that the $BaCO_3$ residue is 85.15% $BaCO_3$, while at 40° approximately 5.24% of the theoretical is converted to CO_2 or for every mol of sugar destroyed, .524 mols of CO2 is produced, calculated on the basis that the $BaCO_3$ residue is 82.8% $BaCO_3$. The 14.8% at 25° and the 17.2% at 40° of the substance in the residue was undetermined.

IV
INTERPRETATION OF RESULTS

The results obtained in this study vary somewhat and rather strikingly from the results from the work of McGrew and Boschult[6]. Both McGrew and Boschult used in the beginning of the experiment six equivalents of NaOH for every mole of sugar. As the reaction proceeded the concentration of the -OH ion decreased. The results they reported show curves similar to the ones produced in this study, except they show no variations in the total combined alkali, the non-volatile and the volatile acids produced. The occurrence of the two irregularities in the curves (Figure II at 25° and but slightly in Figure III at 40°, due undoubtly to the higher temperature) are of interest and are probably due to the formation of intermediate oxidation products. This is assumed because at the first variation in the curves at 25° it is noted that about 75-80% of the sugar had disappeared (Figure IV), and that at this point we find that the shorter chain oxidation products are beginning to predominate as can be seen from the

curves on the percentage completion of the reactions in Fugure V and VI.

From the curves on the completion of the reactions (Figure V and VI) it can be seen that the results show glucose to disappear rather regularly and that there is 95% of the sugar at 25° and 99% at 40°, destroyed at the end of 50 hours, while at 25° with 6 equivalents of NaOH, Boschult found that 72 hours had elapsed before the 95% of the glucose had disappeared.

One of the most striking observations to be noticed in the present investigation is that the percentage completion of the reactions (Figure V and VI) do not coincide as do the curves for the completion of reactions of volatile, non-volatile acids and glucose in the work of McGrew. McGrew assumed that from his results there was one rate of reaction for the oxidation of glucose or a set of simultaneous reactions that acted as one under the conditions that was imposed upon the glucose. The present investigation does not show this to

be the case in a solution of fairly constant -OH ion concentration. The explination of this variation undoubtly lies in the fact that the higher concentration of the -OH ion causes a more rapid shift in the enediols to the 3-4 enediols, thus giving rise to the shorter chain products. This view also bears out the results obtained by determination of the ratios of the mols of volatile and non-volatile acids produced for every mol of sugar destroyed, where it is seen that the volatile acids are far in the excess of the non-volatile acids.

The ratios of the non-volatile and volatile acids produced to the mols of sugar destroyed are given in Table VIII. These values are calculated by taking the mols of the oxidation products produced at the end of the run, while the values given in Table IX are the ratios of the mols of non-volatile and volatile acids produced to the mols of sugar destroyed at a given time. If the values of Table IX are plotted it will be seen that they are not a straight line. In the work of McCrew and Boschult they found that similar values as are

given in Table IX, produced straight lines. This fact also bears out the conclusions that the oxidation of d-glucose in a saturated solution of $Ba(OH)_2$ is not due to a single reaction, but is a series of reactions, each having its own velocity.

In comparing the two Figures, (III and IV) it will be noticed that the glucose has largly disappeared at 40° while the formic has hardly made its appearence. This shows, undoubtly, that the a good deal of the formic comes from the intermediate products.

Boschult found at 25° that for every mol of glucose destroyed, 1.073 mols of volatile, (largly formic) acids were produced. However, calculations of the results of this investigation show 4.40 mols at 25° and 4.45 mols at 40° of volatile acids produced per mol of glucose destroyed. There was found .639 mols at 25° and .652 mols at 40° of non-volatile acids produced per mol of glucose destroyed. .092 mols of CO_2 at 25° and .0524 mols at 40° were also found to be produced. If the mols of the

oxidation products that are formed are sumed up it will be found to be very near the theoretical, e.g., at 25° there are produced 4.40 mols of volatile acids, .639 mols of non-volatile acids and .0220 mols of CO_2 for every mol of sugar destroyed. At 40° the total oxidation products produced are 5.154 mols (4.45 mols of volatile acids, .652 mols of non-volatile acids and .0524 mols of CO_2) per mol of sugar destroyed.

Evans in 1925 showed that the yield of CO_2 was higher in low alkalinities than in high alkalinities. This can be explained by assuming that the 1-2 enediols are formed to a larger percentage in the low concentration of alkali. The present investigation also bears out this fact.

It is doubtful if the oxidation would ever reach the theoretical since there are a number of the short chain oxidation products that are relatively stable under these conditions, although the large production of the oxidation products in a constant -OH ion

concentration seem to indicate that the reactions are largely complete and that if the reactions were carried out for a longer period of time with the maintaining of the constant -OH ion concentration, the reaction might be found to go to the theoretical, i.e., CO_2 and H_2O.

It will be noticed from Table III and IV that the cc's of N HCl needed to neutralize the 50 cc sample (column 3) decreases after a certain point has been reached in the oxidation, although the solution contains anexcess of $Ba(OH)_2$. This is thought to be due to the formation of insoluble $BaCO_3$

The author believes that the present investigation indicates the following conclusions:-

(1) The oxidation shows a tendency to go first to the acids and these in turn are oxidized, probably by breaking off a C-atom at a time.

(2) The percentage completion of the reactions indicate that the longer chain oxidation products are the most unstable and the shorter chain products are the most stable under the conditions of the experiment.

(3) The formation of the large percentage of the volatile acids indicate that the reaction goes largly to the 1,2 and 3 C-chain oxidation products.

(4) The percentage completion curves (Figures V and VI indicate there is not a simgle reaction or a simultaneous set of reactions, but a series of reactions which is to be expected if it is as Nef suggested, a possibility of 116 compounds being formed from a 6 C-sugar.

(5) The transformation of glucose into intermediate compounds is a relatively fast reaction and the other reactions are dependent on it's velocity.

(6) The results of the oxidation of glucose in a saturated solution of $Ba(OH)_2$ at 40° indicated a faster reaction, otherwise the same general results are obtained.

(7) The results as found in the present investigation may be found useful in an interpretation of the oxidation in the animal body where exacting degrees of acidity and alkalinity are maintained.

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